EFFECTS OF LITHIUM IODIDE DOPING ON
THE ASSOCIATED MOLECULAR STRUCTURE OF BROWN COAL.

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ABSTRACT
    Effects of lithium iodide (LiI) doping on the associated
molecular structure of brown coal have been investigated.
Devolatilization of the coal is enhanced with LiI doping at lower
temperature range (<300°C). The devolatilization enhanced with LiI
doping proceeds without thermal decomposition and cleavage of cross-
linkage structure. High temperature ^{1}H-NMR results indicate that the
LiI doping increases the fractions of mobile structure, and also
enhances the mobility of molecules. During heat treatment, LiI
maintains the enhanced molecular mobility resulting in an increase in
the evolution of volatile matter.

INTRODUCTION
    Coal is complex macromolecular compounds containing several
types of noncovalent interactions, such as hydrogen bonding, van der
Waals, aromatic $\pi-\pi$ and charge transfer interaction. Chemical and
physical properties of coal are strongly affected with associated
structure as well as chemical structure of coal molecules. The
associated structure of coal molecules is governed the type and
strength of noncovalent interactions exist in coal. Low rank coals,
such as lignite and brown coal, have a high oxygen content, and a
considerable proportion of the oxygen is present in the form of
carboxyl and phenolic functional groups. These oxygen containing
groups are forming hydrogen bonds with each other resulting in the
associated structure of molecules. Thus, it can be considered that
inter- and intra-molecular hydrogen bonding interactions are responsible
for the properties of low rank coal.
    The role of hydrogen bonding in the properties of coal has
already been recognized. Painter and co-workers [1] have discussed
the band assignment of hydroxyl groups forming hydrogen bonding
interaction in coal. They also discussed the significance of
hydrogen bonding on the structure of coal. The classical solvent
induced swelling techniques of polymer chemistry have been applied to
investigate the associated structure of coal molecules [2-6]. Larsen
et al. [4] estimated that bituminous coal contain about 5 times as
many hydrogen bond cross-link as covalent cross-link. Brenner [3]
pointed out the effects of hydrogen bonding interaction on the glass
transition temperature and glassy properties of coal. The importance
of the hydrogen bonding interaction in the formation and stabilization
of coal macromolecular structure has also demonstrated by computer
aided molecular design technique [7,8].
    Cross-linking reactions at hydroxyl sites during heat treatment
have been postulated to suppress the fluidity and volatile matter
formation of coals [9-14]. Van Krevelen and co-worker [9] provided
direct evidence on the role of hydroxyl groups in suppressing
fluidity by model compound study. The mechanism of the suppression
by the presence of hydroxyl groups has been modeled as involving
cross-linking reactions at hydroxyl sites. The solvent induced
swelling techniques have been employed also to determine cross-link
density changes during heat treatment. The results obtained from the
swelling techniques have demonstrated that cross-linking in low rank
coals occurs prior to tar evolution, and the temperature is lower
than that for bituminous coals [10-12]. Comparison of char solvent
swelling behaviour and gas evolution has indicated that the low
temperature cross-linking occurs simultaneously with CO_2 and H_2O
evolution [13]. The cross-linking at lower temperature was also
inferred with the Proton Magnetic Resonance Thermal Analysis (PMRTA)
[15,16]. The mobile phase of low rank coal determined from NMR

relaxation time decreased at a substantially lower temperature, below that for tar evolution.

In this paper, to clarify the effects of hydrogen bonding interaction on the associated molecular structure of Loy Yang brown coal, the devolatilization of the coal subjected to modification of hydrogen bonding interaction with lithium iodide doping have been investigated by means of a thermogravimetric analysis (TGA), a high temperature electron paramagnetic resonance spectroscopy (HT-EPR) and PMRTA.

EXPERIMENTAL SECTION
Coal Sample and Reagents.
The coal sample used for the present study is Loy Yang brown coal (LY, C;70.6wt%, H;5.0wt%, N;0.8wt%, O+S;23.6wt% diff.). The sample coal was ground to pass through 100 Tyler mesh and dried under a vacuum at 40°C for 24 hours. Methanol (G.R. grade) as a solvent and lithium iodide (G.R. grade) were used without further purification.

Preparation of LiI Doped Coal.
A known amount of lithium iodide (LiI), i.e., 4.17×10^{-3} mol/g-coal, dissolved in methanol was added to dried coal particles. The coal suspension was placed in an ultrasonic bath for 10 minutes and stirred for 2 hours at room temperature. After standing the suspension over night, the solvent was evaporated off. The LiI doped sample thus obtained, was dried under a vacuum at 40°C for 24 hours and then cooled down in a flow of nitrogen.

TGA.
Typically, 10mg of sample in platinum TG cell was placed in a thermogravimetric equipment (ULVAC TGD 5000). The sample was heated at 105°C under a flow of nitrogen for 2 hours to remove moisture. TG curves of the sample were measured at a heating rate of 5°C/min up to 500°C in a flow of nitrogen. For kinetic studies, the sample removed moisture at 105°C was heated at a rate of 200-400°C/min to a prescribed temperature of 200-400°C and kept at final temperature for 30 minutes.

HT-EPR.
The sample in a HT-EPR quartz tube of 6mm o.d. was inserted directly into a cavity where the sample was heated at 105°C in a flow of nitrogen to remove moisture. The variation in EPR spectra was monitored with a Varian E-109 EPR spectrometer equipped with a cylindrical high temperature cavity (Micro-device Co.Ltd.) in a flow of nitrogen at a heating rate of 5°C/min. The details of the HT-EPR operation have been reported previously [17].

PMRTA.
For a PMRTA experiment, 500mg of sample was contained in a 10mm o.d. glass tube and dried at 105°C in a flow of nitrogen prior to analysis with PMRTA. The solid-echo pulse sequence (90°x-t-90°y) was used to generate ^{1}H-NMR transverse magnetization signal. The solid-echo signal, I(t), was recorded at regular intervals (1-2 minute) while the sample was heated from room temperature to 500°C at a rate of 4°C/min in a flow of nitrogen. The details of PMRTA operation have also been reported previously [17].

RESULTS AND DISCUSSION
TGA Studies
The effects of LiI doping on the devolatilization properties of Loy Yang brown coal (LY) were investigated with TGA. TGA curves for LY and LiI doped LY (LILY) are shown in Figure 1 where the weight loss of coal sample is expressed on an ash and LiI free basis. The weight loss of LY starts at about 200°C, and increases gradually with increasing temperature. LILY always shows higher weight loss than that for LY over the range of measurement temperatures. The weight loss of LY increases from 25wt% to 44wt% at 400°C with LiI doping.

In Figure 2, the variation in the differential weight loss curves, i.e., the rates of volatile matter evolution, for LY and LILY are plotted as a function of temperature. The rate of evolution for LY monotonously increases, and reaches a maximum value at 400°C. In contrast, the rate for LILY increases immediately at the initial stage of heating. These results indicate that LiI doped in LY enhances the evolution of volatile matter at lower temperatures. It should be noted that the temperature at which the maximum rate of

volatile matter evolution is obtained shifts down from 400°C to 250°C with LiI doping and the temperature for LILY seems to be much lower than that of thermal decomposition and cleavage of cross-linkage structure in the coal.

For kinetic analysis of the devolatilization, a systematic series of experiments were carried out on change of the yields of devolatilization products (weight loss), Y, with time, t, at different temperature. Considering the appreciable and rapid decrease in the weight of coal, the reactions in early stage appear to proceed mainly with evolution of volatile matter. Figure 3 shows a typical result of analysis where ln(1-Y) are plotted against t assuming a first-order irreversible reaction. In the figure, straight line can be seen within the first 1 minutes, implying that evolution of volatile matter in the early stage can be described by a first-order irreversible reaction.

The first-order reaction rate constant, k, for evolution of volatile matter was obtained analyzing data of Y at different time and temperature for LY and LILY. The Arrhenius plots of these reaction rate constants are shown in Figure 4. It is seen that k's for LILY is higher than k for LY within the present range of reaction temperature, reflecting the promotion of volatile matter evolution by LiI doping. The activation energy, E, for LILY (34.3kJ/mole) is found to be appreciably smaller than that for LY (50.3kJ/mole). This less temperature-sensitive devolatilization may be attributed to the modification of associated molecular structure of the coal with LiI doping

HT-EPR Studies

The spin concentrations for LY and LILY were monitored by using HT-EPR. With HT-EPR technique, relatively stable radicals are detected, such as stable π and/or s radicals with relatively long life. As shown in Figure 5, the spin concentration for LY starts to increase at about 170°C and increases drastically beyond 380°C. The drastic increase in the spin concentration observed beyond 380°C in LY may be attributed to the increase in stable π and/or s radicals produced with thermal decomposition and cleavage of cross-linkage structure during heat treatment [18]. For LILY, however, the spin concentration remains almost constant at temperature below 350°C, where marked increase in weight loss is seen. A drastic increase in the spin concentration similar to that for LY is seen beyond 380°C. This result suggests that the reaction mechanism for weight loss for LILY at lower temperature is somewhat different from that for LY and evolution of volatile matter at lower temperature proceeds without thermal decomposition and cleavage of cross-linkage structure. Since the temperature at which LILY gives the maximum evolution rate is much lower than usual pyrolysis temperature, the enhancement of devolatilization at lower temperature, therefore, might be resulted from the evolution of volatile matter which linked physically and/or noncovalently to the coal.

PMRTA Studies
Residual Hydrogen

The PMRTA technique was employed to elucidate the effects of LiI doping on the thermal transformation behaviour of LY. The initial amplitude of solid-echo signal, I(0), is closely proportional to the hydrogen content in the specimen. Therefore, the variation in I(0) plotted in Figure 6 is akin to that of weight loss (TG curves) in Fig. 1. For LY, I(0) decreases rapidly as heating above 350°C relative to the decrease in weight loss. This fact means that disproportionation of hydrogen in the specimen occurs at this temperature range. From the HT-EPR study, the disproportionation is considered due to the evolution of hydrogen rich compounds, such as methane and water, produced by the thermal decomposition and cleavage of cross-linkage structures. The variation in I(0) for LILY is nearly in accordance with that in the weight loss at temperatures below 350°C (Fig.1), where a significant increase in volatile matter was observed. Thus, it appears that the composite of volatile matter evolved at lower temperature (<350°C) is analogous to that of parent coal (LY). The disproportionation is seen to occur slightly above 350°C.

Mobile Remaining Hydrogen

The separation of the solid-echo signals permits hydrogen-weighted mobile and rigid fractions of the molecular structure in coal [17]. The fractions of remaining hydrogen in mobile structures, H_m, on the

basis of the initial amplitude of signal are plotted in Figure 7 against temperature. H_m for LILY is high even at the initial stage of heating, increases with temperature, and then reaches a maximum value at about 150°C. On further heating, H_m maintains the high value up to 400°C where evolution of volatile matter occurs. The result indicates that the LiI doping increases the fraction of mobile structures in LY and keeps it at the higher level up to 400°C. H_m for LY shows a maximum value at about 320°C, and then decreases rapidly on further heating. For LY, the drastic increase in the spin concentration (>380°C) and the rapid decrease in I(0) (>350°C) were observed at a higher temperature range. The rapid decrease in H_m, therefore, could be attributed not only to the evolution of volatile matter, but also to the condensation and recombination reactions, which follow the thermal decomposition and cleavage of cross-linkage structures in coal.

CONCLUSIONS
1. Devolatilization of LY is enhanced with LiI doping at lower temperature range (<300°C).
2. The activation energies for the devolatilization decrease with LiI doping. This less-temperature sensitive devolatilization may be attributed to the modification of associated molecular structure of the coal with LiI doping.
3. The devolatilization enhanced with LiI doping proceeds without thermal decomposition and cleavage of cross-linkage structure.
4. The doping LiI increases the fractions of mobile structure, and also enhances the mobility of LY molecule.
5. During heat treatment, LiI maintains the enhanced molecular mobility resulting in an increase in the evolution of volatile matter.

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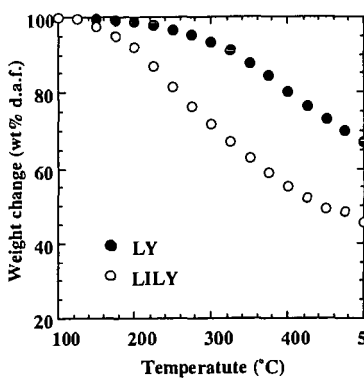   No.5;Elsevier:Amsterdam,Netherlands,1983;71

Figure 1. Effects of LiI doping on the
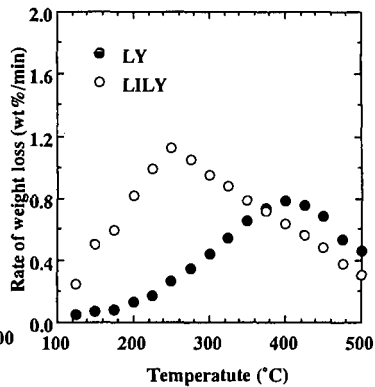devolatilization properties of LY

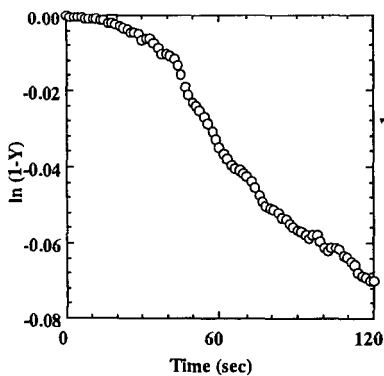

Figure 2. Differential weight loss curves
for LY and LILY

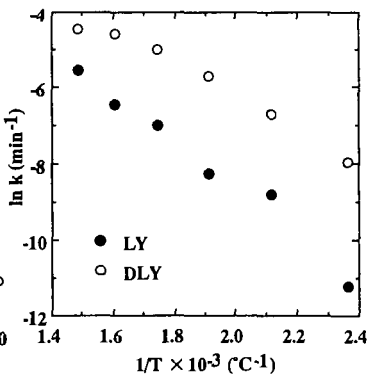Figure 3. Varistion of ln(1-Y) against
reaction time for LILY at 250°C

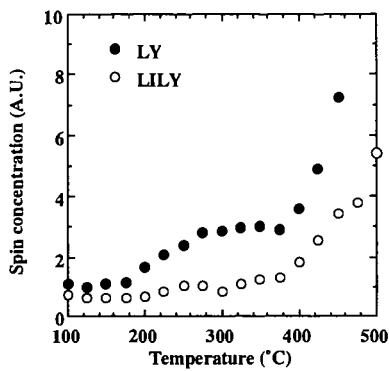Figure 4. Arrhenius plots of weight loss
rate constants for LY and LILY

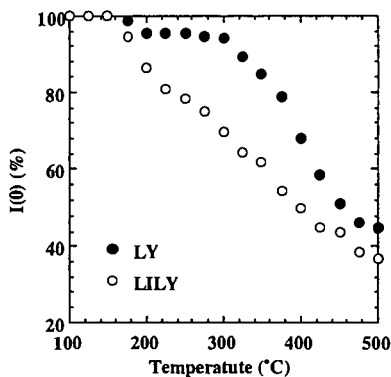**Figure 5.** Variation in spin concentration for LY and LILY

Figure 6. Residual hydrogen, I(0), pyrograms derived from PMRTA data for LY and LILY
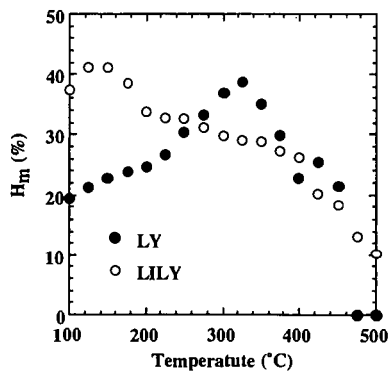

Figure 7. Mobile remaining hydrogen, Hm, pyrograms derived from PMRTA data for LY and LILY